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TITLE: “SYNTHESIS OF AMIDE FUNCTIONALIZED CARBON NANOTUBES”

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Synthesis and Characterization of Amide-InterConnected
Single-Wall Carbon Nanotubes

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Abstract

A covalent, amide-bond interconnection between functionalized single-wall carbon nanotubes (SWNTs) is reported. SWNTs covalently connected via an amide bond were prepared by coupling the carboxylic acid group from one SWNT with the amine group on a different SWNT using DMAP and DCC reagents. The SWNT material was characterized by ATR FT-IR, Ramen Spectroscopy and Thermogravimetric Analysis (TGA). The amide functionalized SWNTs have potential to make polymeric-like materials and have applications in high strength nanocomposites.

Introduction

Single-wall carbon nanotubes (SWNTs) are amazing materials that have interesting physical properties and the potential to be incorporated into a wide variety of technological applications.[1] Carbon nanotubes are currently being used as chemical sensors[2,3,4,5] and SWNTs have been incorporated into nanoassemblies and reinforced polymer composites.[6,7] Covalent functionalization of carbon nanotubes in a controlled manner plays a central role in tailoring the properties of SWNT devices.[8]

The development of functionalization methods for carbon nanotubes is of fundamental importance for gaining a greater knowledge of chemical reactivity for materials with nanoscale size. Functionalization of SWNTs could lead to advances in nanodevice applications.[9,10] Suitable functionalization could enable the linking of individual carbon nanotubes to form complex networks for nanoscale electronic circuits.[11] Coupling of functional groups to SWNTs has almost exclusively been achieved using ester or amide linkages and amides have been the primary linkage method for nanotube interconnects.[12]

A simple and scaleable synthesis of covalently interconnected SWNTs through an amide groups is reported. The preparation of amide-connected nanotubes uses mild DMAP/DCC coupling of carboxylic acid-functionalized SWNTs and amine-functionalized SWNTs.[13,14,15] The interconnection of carbon nanotubes via chemical functionalization has been reported.[9,11,16,17,18,19] However, in the previous experiments the SWNTs have been connected by using a single type of functionalized SWNT with a spacer group to form the amide bond. The formation of a covalent interconnection between SWNTs without incorporating a spacer group could potentially change the electronic properties of the materials and lead to polymer-like SWNTs that could be used to make novel nanocomposites. The intermediates and products were characterized by ATR FT-IR, Raman spectroscopy and thermogravimetric analysis (TGA).

Experimental Section

Measurements. Attenuated total-reflectance (ATR) Fourier transform infrared (FT-IR) spectra were obtained with a Thermo IR100 spectrometer. Raman spectra were acquired using the samples in the solid state in the backscattering mode on the microstage of a Horiba Jobin Yvon LabRm spectrometer. Spectra were recorded over the range of 100-3000 cm^{-1} and an excitation wavelength of 632.8 nm. Thermogravimetric analyses (TGA) were carried out on a TGA 2050 thermogravimetric analyzer with a heating rate of 10 ^{o}C/min and argon flow (20 mL/min).

SWNT-COOH (2): The SWNTs (1) used in this study were purchased from Carbon Nanotechnologies, Inc. The catalyst (support and metal particles) was removed by sonicating the purchased SWNTs in 37 wt% HCl for 30 min, leaving them in acid overnight and diluting with deionized water followed by filtration through a 0.2 m membrane filter. The SWNTs (1) were readily converted to the SWNT-carboxylic acid under strongly acidic conditions.[20] Initially, 100 mg pure SWNTs were treated with a mixture of 3:1 concentrated H_2SO_4/ concentrated HNO_3 (60 mL and 20 mL, respectively) and 500 mL of distilled water and then placed in an ultrasonic cleaner for 1.5 h. This solution was then filtered and dried at room temperature and added to a solution of 4:1 sulfuric acid/ hydrogen peroxide (40 mL and 10 mL, respectively) and sonicated for 10 minutes. The solution was then placed under vacuum filtration, the SWNT-COOH product was collected, and the SWNTs were dried overnight at 80 ^{o}C under vacuum. Both the purification process and the shortening process terminate the open ends and sidewall defect sites of the SWNTs with carboxylic acid groups.[21,22,23] Using the titration method of Haddon *et al.*,[24] the number of acidic sites on the purified SWNT-COOH was determined to be approximately 9.6-11%.

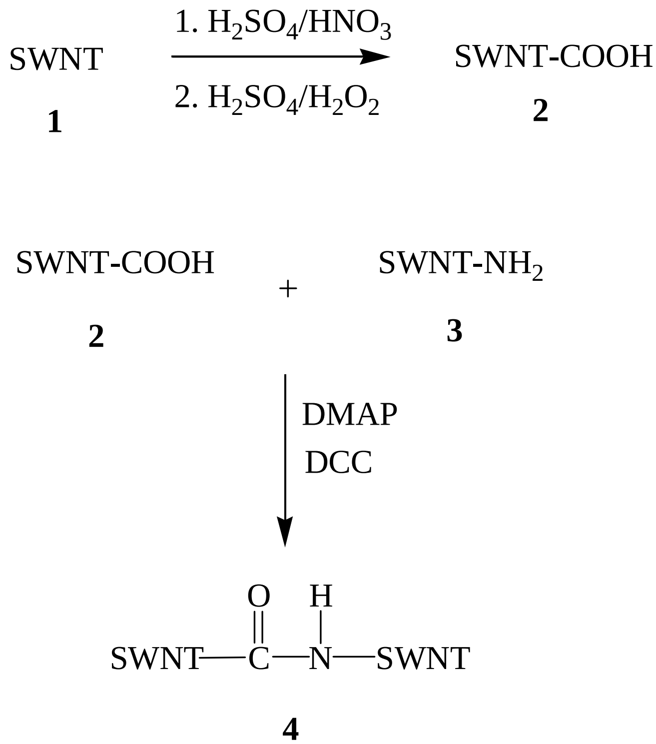
SWNT-NH$_2$ (3): The amine terminated carbon nanotubes were synthesized by a novel procedure.[25] The SWNT-NH_2 was isolated then dried overnight at 80 ^{o}C under vacuum.

SWNT-NHCO-SWNT (4): SWNT-COOH (61 mg) and SWNT-NH_2 (57 mg) were mixed with 20 mL of DMF and sonicated for 1 hour. After sonication, 100 mg of DMAP and 10 mL of DMF were added to the solution and the solution was sonicated for 5 min. DCC (250 mg) was then added and the entire solution was placed on an oil bath at 80 ^{o}C under argon for 4 days.[26] The resulting SWNTs were then filtered, washed with methanol, and then placed in a round bottom flask and dried under vacuum at 80 ^{o}C overnight.

Results and Discussions

The process of using carbodiimide-activiated coupling, which only requires mild temperature conditions, was particularly useful in the coupling of the SWNTs**.** The starting materials and the resultant covalently interconnected amide SWNTs were characterized with Attenuated Total Reflectance (ATR) FT-IR, which has been readily used in the study of SWNTs to identify functional groups present on the tube walls.[27]

Scheme 1



The FT-IR spectra for the carboxylic acid (**2**) and amine (**3**) starting materials are shown in Figure 1. The spectrum for SWNT **4** (Figure 2) showed significant functional group presence and compared very well to previously synthesized amide SWNT structures. [28] The 1666 cm^{-1} stretch can be accredited to a amide C=O stretching vibration, the 1602 cm^{-1} peak to the amide N-H deformation, the 1535 cm^{-1} stretch to an amide C-N stretching vibration, the 1462 cm^{-1} stretch to an amide N-H bending, the 1336 cm^{-1} stretch to the amide C-N stretching, and the 1261 cm^{-1} stretch to the amide out-of-plane N-H deformation. The stretches located at 1764 cm^{-1} and 1408 cm^{-1} can be credited to the unreacted carboxylic acid C=O stretching vibration and O-H in-plane bending, respectively.

Identical FT-IR spectra were obtained from the coupling reaction between acid chloride-functionalized SWNT with the amine-functionalized SWNT. This procedure was not pursued further due its use of the toxic thionyl chloride reagent, the additional step in synthesis and significant coupling was obtained using the mild DMAP/DCC methodology. The reaction of

SWNT-COOH (**2**) and SWNT-NH_2 (**3**) without DMAP/DCC reagents was also investigated to confirm the nature of the amide bond between the SWNTs. No SWNT derivatives were obtained under these conditions thus excluding any hypothesis of non-covalent linkages, such as salt formation.

The amide-interconnected SWNTs **4** were also characterized via Raman Spectroscopy (Figure 3). The Raman scattering spectra clearly show the typical resonant Raman peaks inherent for SWNTs.[29] The functionalization of the SWNTs introduced many sp3 hybrids and the disorder band (D-band, 1290 cm^{-1}) became much larger compared to the pristine carbon nanotubes. The disorder band does not change for noncovalent functionalizations unless the process brings some new defect sites to the sidewalls of the carbon nanotubes. Heating the amide functionalized SWNT (**4**) in argon to 800 ^{o}C at the rate of 10 $^{o}C/min$ in a TGA system dramatically reduced the intensity of the sp3 carbon mode at ~1290 cm^{-1} in the Raman spectrum of the material collect after pyrolysis. This result indicates the defunctionalization of the SWNT takes place upon heating, which is consistent with the thermal degradation properties of other functionalized SWNTs. The intensity of the D-band (1290 cm^{-1}) was divided by the intensity of the tangential mode (G-band) at 1590 cm^{-1} and this ratio provides a good indication of the relative degree of functionalization of approximately 13%.[30]

Additional evidence for covalent interconnection of amide groups and the degree of functionalization was provided by thermal degradation analysis (TGA). Figure 4 shows the TGA data for SWNT-COOH, SWNT-NH_2 and SWNT 4 at a heating rate of 10 $^{o}C/min$ in the presence of argon. The TGA analysis shows a major decline in mass for the amide-interconnected nanotubes between the 200 ^{o}C to 400 ^{o}C region. Weight loss due to functionalization can be seen from the TGA tests and the results showed that total weight loss of about 25% is observed for the dissociation of the amide groups. A weight loss of 25% is equal to approximately a degree of functionalization of one addend in every 50 carbons. The number of SWNTs linked via the amide bonds and the position of the interconnections (side-wall versus end-wall) are currently being investigated.

Conclusions

Single-wall carbon nanotubes were functionalized with carboxylic acid and amine functional group then they were coupled using the mild DMAP/DCC conditions to form novel, amide-linked SWNTs. Through FT-IR spectroscopy, Raman spectroscopy and TGA analysis it was proven that the intermediate compounds were successfully covalently interconnected without a spacer group. The amide connected SWNTs have the potential to be used in nanocomposites and form interesting polymeric assemblies.

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